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Structure determination from powder diffraction

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The review surveys modern methods for the determination of unknown crystal structures of organic and inorganic compounds from powder diffraction data. The main stages of this process, from the preparation of the specimen to a search for the structural motif followed by the Rietveld refinement, are considered. The results obtained on different diffractometers using X-ray, synchrotron, and neutron radiations are demonstrated to be well reproducible. Examples of successful structure solution are cited, which provide evidence that powder diffraction is a reliable tool in establishing structures of a wide range of compounds for which single crystals are unavailable.

Key words: powder diffraction, crystal structure, Rietveld method.

The use of X-ray structure analysis for the determination of three-dimensional atomic arrangements in crystal structures of organic and inorganic compounds is an important stage both in the design of new substances and in the development of new procedures for the synthesis of the already known compounds. The chief drawback of X-ray structure analysis is the need for high-quality single crystals of substantial dimensions, which sometimes presents an impenetrable barrier to researchers. Unfortunately, finely dispersed crystalline powders of required compositions are often obtained instead of desirable single crystals. However, new modern methods for the structure determination from powder data allow one to reliably establish crystal structures of compounds containing up to 30 and sometimes more nonhydrogen atoms per asymmetric unit. The previously unknown structures of compounds solved for the first time from powder diffraction data appear in an ever increasing number.[1,2] These compounds belong to different classes both of inorganic (high-T_c superconductors, magnetics, solid electrolytes, and zeolites) and organic (dyes, pharmaceuticals, physiologically active substances, *etc.*) materials. Numerous research groups working in universities and industrial laboratories actively use methods for the structure determination from powder diffraction (SDPD) and obtain reliable data.

The development of the full-profile refinement (or the Rietveld method)[3,4] had a great impact on the progress of methods for the structure determination from powder data. The structure determination[5] of the complex $(NH_4)_4[(MoO_2)_4O_3](C_4H_3O_5)_2 \cdot H_2O$ in which the modern scheme of structure completion from powder diffraction data has successively been employed for the first time made a significant contribution to the evolution of powder X-ray diffraction analysis. This structure solution included indexing, the determination of integrated intensities of 120 reflections, the search for two heavy Mo atoms by the Patterson method, the localization of the remaining atoms from Fourier syntheses, and the final Rietveld refinement. It was demonstrated[6—20] that reliable results can be obtained for a wide range of compounds. Presently, the structure determination from powder data is the focus of attention as a tool in establishing structures in the absence of single crystals. Various aspects of SDPD were analyzed in a series of reviews.[2,21—39]

The present review surveys the main stages of the structure determination from powder diffraction data, beginning with the preparation of the specimen and ending with the structure solution followed by the refinement, and gives various examples of its successful use. The main aim of the review is to demonstrate the broad scope of the powder X-ray diffraction methods and to give an idea of problems, which one may face when employing these methods.

Main stages of structure determination from powder data

By the structure determination from powder data (SDPD) is meant methods, which allow one to establish the crystal structures of compounds available only as polycrystalline powders. The crystal structures can be established based on conventional X-ray data as well as on synchrotron and neutron diffraction data. (Hereinafter, an X-ray pattern measured on a powder diffractometer will be referred to as a powder pattern.)

Main stages of SDPD are presented in Scheme 1. It should be noted that this division is rather arbitrary because the stages are interrelated rather than completed procedures. For example, the second stage of investigation often reveals the fact that the resulting

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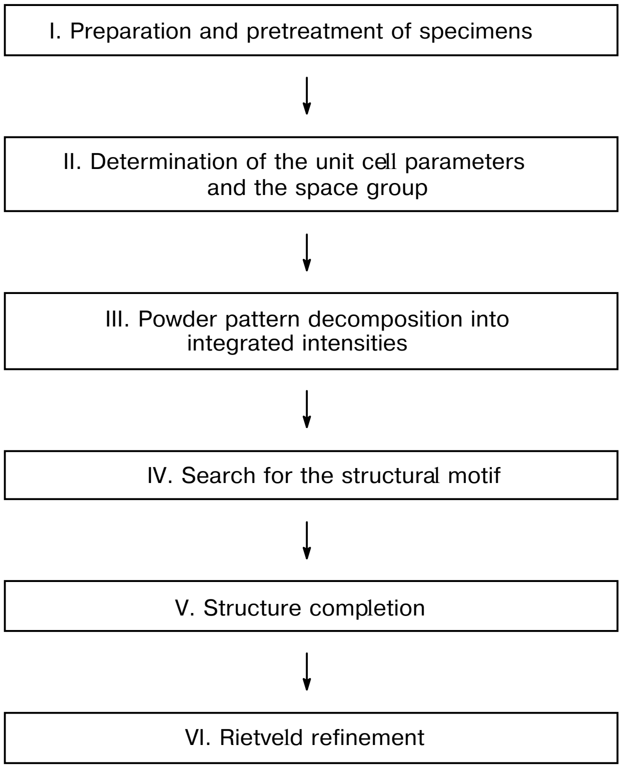
specimen is non-single-phase and contains impurities in amounts unsuitable for further studies due to which researchers have to return to the first stage. The stage II often does not allow the unambiguous determination of the unit cell parameters and/or the space group; instead, several possible alternatives are obtained. Hence, researchers are faced with examining all these alternatives at the stage III, which often enable them to find the only correct solution. In some cases, the true unit cell parameters and/or the space group can be unambiguously determined only at the stage VI, and hence, the stage II is completed simultaneously with the structure solution and refinement. The above-considered examples show that the structure determination from powder diffraction data is not actually a direct sequence of individual stages (see Scheme 1). This procedure is much more complicated and can involve a large number of internal stages when the results of a particular stage send researchers returning to one of the previous stages rather than allow them to proceed to the next stage.

Scheme 1



Procedures for measuring powder patterns are not presented in Scheme 1. In general, one need only to carry out two measurements, *viz.*, before the stage II (to determine the unit cell parameters) and after the stage II (to solve and refine the structure). However, additional measurement are often required, which will be discussed in the detailed consideration of particular stages.

I. Preparation and pretreatment of specimens

In the stage I of SDPD, it is desirable to solve at least the following three problems: 1) to synthesize a compound in an amount, which is sufficient to obtain high-quality diffraction data; 2) to prepare a one-phase specimen, *i.e.*, a specimen free from impurities and contaminating phases wherever possible, but failing this, impurities should be studied as thorougly as possible by other physicochemical methods and based on analysis of the synthetic scheme; 3) to estimate the stability of the compound under the conditions of X-ray data collection.

Based on the information obtained, a researcher can design the diffraction experiment. For example, if the amount of the compound at hand is only several tens of milligrams, neutron diffraction studies, which require at least hundreds of milligrams of the specimen, cannot be performed. The above-mentioned amount of a compound is also often insufficient for investigation on some laboratory diffractometers. If the compound is in addition air-unstable and must be stored in a sealed cell or capillary, the experiment should be performed using synchrotron radiation or a high-intensity rotating anode X-ray tube. One have to solve analogous problems in the design of diffraction experiments in the cases of non-single-phase substances or molecular compounds consisting of a large number of atoms.

The adjustment of the diffractometer and the preparation of the specimen are of importance in diffraction studies. In synchrotron or neutron diffraction experiments, these jobs are generally executed by skilled operators, whereas different users perform these operations in studies on laboratory X-ray diffractometers. Problems of the adjustment of laboratory diffractometers and the preparation of specimens were covered comprehensively in handbooks.[40—43] These problems were also discussed in a number of papers devoted to the structure solution from powder diffraction data (see, for example, Refs. 44—48).

II. Determination of the unit cell parameters and the space group

Generally, the determination of the unit cell parameters requires a special diffraction study on a high-resolution device. Of laboratory devices, diffractometers equipped with a curved monochromator, which cuts off the Kα_2 component of the characteristic radiation, are best suited for these purposes. The resulting powder patterns can be stored either on X-ray films, which show each reflection having a non-zero intensity as a shaded band, or in a computer file as tabular values of $2\theta_i$ and y_i ($2\theta_i$ is the angle between the directions of the detector and the incident beam and y_i is the measured intensity of scattered radiation at a given position of the detector). These data can be conveniently summarized in graphical form. As an example, the fragment of a powder pattern of $C_{10}H_{17}N_7O_2$ is shown in Fig. 1.[49] The

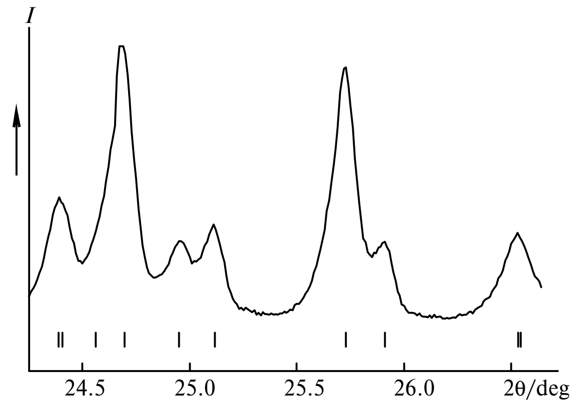


Fig. 1. Fragment of the powder pattern of $C_{10}H_{17}N_7O_2$.[49] The calculated positions of the 2θ reflections are indicated by vertical bars.

position of the maximum of each reflection $(2\theta)_p$ (these maxima are indicated by vertical bars at the bottom of Fig. 1) characterizes a particular series of atomic planes in the powder under study according to the Bragg law

$$2d\sin\theta = n\lambda, \tag{1}$$

where λ is the wavelength, $\theta = \theta_p$, and d is the d space (interplanar distance).

Generally, the intensity maxima or peaks in a powder pattern are searched for and their positions are determined using standard diffractometer software. However, it is worthwhile to additionally examine the results of the automatic search for peaks by a visual inspection. With a set of peaks $(2\theta)_p$, one can determine the $\{d_p\}$ spaces for the compound under study according to Eq. (1). If the unit cell parameters (a, b, c, α, β, γ) are known, each system of atomic planes in the crystal can be characterized by a three-dimensional set of integer *hkl* indices. All these parameters are related by the following equation:

$$d(hkl) = (h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2hka^*b^*\cos\gamma^* + 2hlb^*c^*\cos\beta^* + 2klb^*c^*\cos\alpha^*)^{-0.5}, \tag{2}$$

where a^*, b^*, c^*, α^*, β^*, and γ^* are the parameters of the reciprocal lattice.[50] Hence, in the study of an unknown structure, it is necessary to determine the unit cell parameters a, b, c, α, β, γ and the *hkl* indices based on the $\{d_p\}$ spaces so that Eqs. (2) are valid for the total $\{d_p\}$ set. This procedure for the search for the unit cell parameters and integer *hkl* indices is called indexing.

In spite of the simple formulation, the problem of indexing is rather complicated because the positions of the peaks $(2\theta)_p$ carry errors (either random or systematic) and sets of peaks are not necessarily complete (for example, weak reflections with intensities close to zero are sometimes absent). In addition, if the $(2\theta)_p$ set contains peaks belonging to impurities, the routine problem of indexing (using the available programs) can turn out to be intractable.

Fortunately, many of the above-mentioned problems have long been known and are well studied,[51] which allowed the development of efficient programs for autoindexing, such as ITO,[52] TREOR,[53] and DICVOL.[54] Each of these programs is based on their own algorithms for indexing. When processing the same data set, only one of the above programs, as sometimes happens, works well. For all programs to give relaible data, a high quality of the set of peak positions is required, *viz.*, the $(2\theta)_p$ values must be determined with an accuracy of 0.03° or better. To take into correct account the possible systematic error associated with the uncertainty of the absolute "zero" position of the detector resulting in the shift of all $(2\theta)_p$ by the same value, a small amount of the standard specimen (for example, of polycrystalline silicon with the cubic unit cell parameter a = 5.4309 Å) is added to the powder under study. With Cu-Kα_1 radiation (λ = 1.5406 Å) and in the absence of the systematic shift of the angles, this standard specimen gives intense reflections at 2θ = 28.45° (the 111 reflection) and 47.30° (220). A comparison of the 2θ angles for the reflections of silicon observed in the experimental powder pattern with the tabular values enables one to estimate the systematic "zero" shift and to apply the corresponding correction to the set of $(2\theta)_p$.

The quality of the solutions obtained by indexing can be estimated using various criteria. The commonly accepted criteria are the numerical characteristics M_{20} (see Ref. 55) and F_{30} (see Ref. 56), which take account both of the deviations of the calculated peak positions from the experimental values and the volumes of the proposed unit cells (the smaller the volume the more reliable the indexing, all other factors being the same). It is agreed that the indexing is reliable if 20 nearest small-angle peaks of the proposed unit cell correspond to $M_{20} > 20$. If the molecular formula of the compound under study is known, the volume of the proposed unit cell often serves as an additional criterion. The latter criterion is particularly useful in studies of the structures of molecular compounds. In molecular crystals, the volume increments of nonhydrogen atoms, which are equal to the ratio of the unit cell volume to the number of the nonhydrogen atoms per unit cell, are 15—18 Å^3. Knowing the molecular composition of the compound under study, it is possible to evaluate the volume per molecule. For example, if the indexing gives a monoclinic unit cell as the solution, its volume would be expected to be a multiple of an even number of the molecular volumes provided that the molecule has no local symmetry.

The procedure for the indexing of powder patterns of inorganic compounds is rather complicated. In this class of compounds, superstructures (giving rise to weak additional reflections) are rather common and it is not unusual to observe small distortions of the unit cells and modulated structures, which are hardly noticeable in powder patterns. Hence, whenever possible, it is desirable to carry out additional electron diffraction investigations of inorganic compounds with the aim of revealing diffraction peaks resulted from various distortions.

The available programs for indexing[52—54] were designed for single-phase substances although they have possibilities for automatic rejection of peaks corresponding to impurities. Attempts were made to design programs, which could allow the indexing of sets of the peak positions measured from multiphase compounds (for example, the AUTOX program[57,58]). However, in the case of a non-single-phase substance, it is worthwhile to make an effort to reject impurity reflections rather than to rely only on such programs. In particular, this goal can be achieved by comparing the peaks derived from the $\{d_p\}$ or $\{(2\theta)_p\}$ set with those of the known compounds available in the PDF2 (Powder Diffraction File) database.[59] The identification of an impurity makes it possible to eliminate all its diffraction peaks from the data set.

The question arises as to the possibilities of modern procedures for indexing. It is assumed[34] that a triclinic unit cell with a volume of up to 1500 Å^3 can be reliably determined based on the experimental data measured, for example, on a Guinier camera. The parameters of larger unit cells can also be determined provided that the crystal system is higher or powder patterns are measured using synchrotron radiation. It is hard to indicate the exact scope of applicability of the modern procedures for indexing. For example, successful indexing was carried out for rhombohedral unit cells with the volumes of 417860 Å^3 (a = 81.28, c = 73.04 Å) and 213424 Å^3 (a = 80.97, c = 37.59 Å)[60] using the ITO [52] and DICVOL programs,[54] respectively. Since the above-mentioned programs[52—54] are not intended for operations with such large unit cells, the $\{d_p\}$ spaces determined in the synchrotron experiments were initially decreased by a factor of 10 and then the resulting unit cell parameters were multiplied by 10.

At the stage of indexing, it is often possible to determine the space group of the compound under study. Here, the major criterion, as in the case of single crystals, is the presence of systematic absences, *i.e.*, the absence of reflections with particular indices. For example, the $0k0$ reflections with odd k must be absent in diffraction spectra of compounds with the space group $P2_1$. However, it should be taken into account that when performing X-ray powder diffraction study, one have to make conclusions about systematic absences based on a limited number of reflections and, hence, the probability of the chosen space group being in error is much higher than in the case of single crystals. In the structure determination from powder data, it is, in general, more correct to speak about the probability of the occurrence of a particular space group belonging to a certain set.[61]

The determination of a small set of the possible unit cells and space groups can be considered as a good result obtained at the stage II (see Scheme 1). At most, researchers succeed in choosing the only unit cell and the only space group.

III. Powder pattern decomposition into integrated intensities

If the results of the first two stages unambiguously indicate that the specimen under study is single-phase and the unit cell parameters and the space group are reliably determined, one can proceed to analysis of the crystal structure of the compound. For this purpose, a precise powder pattern is required. This powder pattern will be used in all subsequent stages. It is necessary to carry out these measurements on diffractometers characterized by the highest possible resolution of all devices to which a researcher has access. It is also desirable to choose as large scan range as possible and a small 2θ scan step (0.01° or smaller). The time of collection of the powder data of the required quality on a laboratory diffractometer is comparable with the time of data collection on four-circle diffractometers equipped with a point detector, which are used in single-crystal X-ray diffraction analysis. When preparing a specimen and choosing the geometry of data collection, one should make efforts to minimize texture effects (these effects are considered below). The requirements on the diffraction data measured before the stage III are identical with those imposed upon the powder patterns used in the Rietveld refinement. These requirements are well known.[62,63]

Let us consider the Rietveld method in more detail.[3,4] In this method, the calculated intensity of the diffraction spectrum y_{calc} at each point i is described by the following formula:

$$y_{\text{calc}}(i) = \Sigma(LPA)_{hkl}f(2\theta_i - 2\theta_{hkl})F_{hkl}{}^2m_{hkl}Y_{hkl} + B(i), \quad (3)$$

where L is the Lorentz factor, P is the polarization factor, A is the absorption correction for a specimen, f is the peak shape function, $2\theta_i$ is the angle corresponding to the measurement at the point i, $2\theta_{hkl}$ is the angle corresponding to the peak position of the hkl reflection, F_{hkl} is the structure factor, m_{hkl} is the multiplicity of the hkl reflection, Y_{hkl} is the texture correction multiplier for the hkl reflection, and $B(i)$ is the background function.

In Eq. (3), summation is carried out over all hkl reflections. Equation (3) is used in the minimization of the functional

$$\sum_{i=1,\ldots,N} w_i\Big[y_{\text{exp}}(i) - Sy_{\text{calc}}(i)\Big]^2 \to \min, \quad (4)$$

where N is the number of measured points, $y_{\text{exp}}(i)$ is the observed intensity at the point i, $y_{\text{calc}}(i)$ is the intensity at the point i calculated according to Eq. (3), S is the scale factor, and w_i is the weighting coefficient, generally, $w_i = y_{\text{exp}}{}^{-2}(i)$.

In the Rietveld method, the minimization of functional (4) involves the refinement of various parameters among which are, in particular, the atomic parameters (*i.e.*, the positions of the atoms in the unit cell and their temperature factors), used in calculations of $F_{hkl}{}^2$. However, from Eq. (3) it follows that functional (4) can be minimized by refining directly F_{hkl}^2 instead of the atomic parameters, provided that the unit cell parameters and the space group, which determine the list of the allowable *hkl* reflections and their $2\theta_{hkl}$ positions, are known. Pawley[64] was the first (in 1981) to minimize functional (4) using F_{hkl}^2 as refinable parameters to verify the correctness of the chosen unit cell and space group. The set of F_{hkl}^2 thus obtained actually corresponds to a single-crystal set of squared structure factors to which conventional procedures for the structure solution, such as the Patterson method or direct methods, can be applied. This is true, but only in ideal cases when peaks of nonequivalent reflections are well resolved. In practice, the situation is different, *viz.*, systematic or accidental overlappings of some peaks are observed, the frequency of these overlapping peaks increases as the 2θ angle increases. In the case of the systematic overlapping typical of high-symmetry structures, the diffraction angles for some groups of nonequivalent *hkl* and *h′k′l′* reflections completely coincide, *i.e.*, $2\theta(hkl) = 2\theta(h'k'l')$. For example, this situation is observed for the *hkl* and *khl* reflections in the tetragonal groups with the Laue symmetry $4/m$. In the case of accidental peak overlapping, the 2θ angles of two or more reflections are so close that these reflections virtually coalesce into one peak. It is evident that F_{hkl}^2 for overlapping reflections correlate essentially with each other. Such correlations, which often lead to negative values of some F_{hkl}^2, substantially impair the reliability of the $\{F_{hkl}^2\}$ set extracted.

In 1988, Le Bail[65] developed another procedure for the determination of the $\{F_{hkl}^2\}$ set by the minimization of functional (4). In the latter procedure, F_{hkl}^2 are calculated using an iteration procedure (unlike the Pawley fit[64] in which each F_{hkl}^2 is refined). This approach makes it possible to stabilize the minimization of functional (4) and, what is also important, to accelerate the process because squared structure factors are not among the refinable parameters. However, in spite of the evident advantages, the Le Bail fit does not solve the problem of peak separation.

Let us revert to the stage III. The minimization of functional (4) according to the Pawley or Le Bail fits is called the powder pattern decomposition into the sum of integrated intensities. This process, which is realized in different programs, including ALLHKL,[64] CSD,[66] EXTRA,[67] FULLPROF,[68] GSAS,[69] LSQPROF,[70] MRIA,[71] PROFIL,[72] and WPPF,[73] performs several useful functions. First, this process, as noted by Pawley,[64] enables one to estimate the reliability of the unit cell parameters and the space group determined previously, which is particularly useful in choosing the correct indexing of the powder pattern out of several possible versions. Second, a researcher obtains a "single-crystal" set of squared structure factors F_{hkl}^2. Third, this procedure gives a set of the reliability factors R_p and R_{wp}, which are also of importance (these factors will be considered below in the discussion of the Rietveld method). The R_p and R_{wp} values determined in the stage III are the smallest possible values, which can be achieved for this powder pattern by minimizing functional (4) with the given unit cell parameters and space group. These reliability factors can serve as a criterion in the final refinement of the structure at the stage VI.

As mentioned above, overlapping of the adjacent reflections is the main factor, which hinders the extraction of a $\{F_{hkl}^2\}$ set from a powder pattern. It is not clear how to redistribute the integrated intensity of a peak among the squared structure factors of overlapped reflections. This is most commonly done using the equal distribution of intensities between overlapping reflections so that the sum of equal F_{hkl}^2, taking into account the multiplicity of each reflection and the Lorentz and polarization factors, is equal to the integrated intensity of the resulting peak. More sophisticated approaches to the solution of this problem are also available.[70,74—82] However, the problem of separation of intensities of overlapping peaks still remains to be solved in a general form.

IV. Search for the structural motif

It is reasonable to suppose that single-crystal methods, such as the Patterson or direct methods, can be applied to the search for the structural motif based on the $\{F_{hkl}^2\}$ set obtained after completion of the stage III. Actually, this approach is often used with success, particularly, if the number of atoms per asymmetric unit as well as the number of overlapping reflections are relatively small. However, the use of single-crystal methods for the determination of the structures of compounds, which are of most interest from the scientific or technological standpoints, more often than not, cannot provide the reliable starting model. In addition, one should remember that the $\{F_{hkl}^2\}$ set obtained from a powder pattern can be distorted by texture effects. In powder patterns measured for organic molecular compounds, the intensities of reflections often sharply decrease as the scattering angle increases, and diffraction peaks for reflections with $d_{hkl} < 1.4$—1.5 Å are virtually not observable against the background. At the same time, it is known[83] that the reliable determination of the structural motif of organic compounds by direct methods based on single-crystal data requires the $\{F_{hkl}^2\}$ set measured up to at least $d_{hkl} = 1.1$ Å.

The above-mentioned difficulties, which restrict the application of direct methods and, to a lesser extent, of the Patterson method, gave impetus to studies devoted to the development of alternative approaches to the determination of crystal structures from powder diffraction data, which were started in 1990s. An important feature of these new methods is the efficient use of *a priori* information on possible structural fragments of the compound under study. The powder data differ fundamentally from the those obtained for single crystals in that the number of reliable values determined from powder data, which are used in the subsequent structure solution, is substantially smaller. In this situation, it is reasonable to try to compensate this lack of data by a decrease in the number of the sought-for structural parameters. For example, if a molecular compound contains 50 nonhydrogen atoms per asymmetric unit, it is necessary to determine the coordinates (x, y, z) of these atoms, *i.e.*, 150 parameters. However, if the molecular structure is known but its position and orientation in the unit cell are unknown, it suffices to find only six parameters or degrees of freedom (three orientational and three translational parameters). In this way, the number of the parameters is decreased by a factor of 25. This sharp reduction of the number of the sought-for parameters provides the basis for new methods, which make it possible to substantially extend the scope of SDPD.

Direct methods. Direct methods[84,85] for the determination of crystal structures employing statistical relations between the phases of reflections are well developed and serve as a reliable tool in the crystallography. For example, these methods enable one to establish protein structures containing up to 2000 nonhydrogen atoms based on single-crystal X-ray diffraction data.[86] Direct methods are realized in the SHELXS97,[83] SIR,[86–88] MULTAN,[84,89] SnB,[90] TEXSAN,[91] MITHRIL,[92] *etc.* program packages devised for single crystals. These programs are of practical interest in the structure determination from powder data because they can be applied to $\{F_{hkl}^2\}$ sets extracted from powder patterns at the stage III. There are also programs employing direct methods and designed for the structure determination from powder data, *viz.*, SIRPOW.92,[79] POWSIM,[93] and CSD.[66] The main advantages of these special-purpose program packages are ingenious algorithms for the separation of overlapping peaks in the stage of application of direct methods. The maximum entropy technique[94–100] can be considered as a modification of direct methods. The latter procedure is realized, in particular, in the MICE program. A prominent demonstration of the possibilities of direct methods, as applied to powder data, is the determination of the crystal structure of sulfathiazole polymorph V $C_9H_9N_3O_2S$,[101] which contains two molecules per asymmetric part of the monoclinic unit cell with a volume of 2285 Å^3. The structure was solved by direct methods using the SIRPOW.92 program based on synchrotron powder data.

Patterson method. Compared to direct methods, the Patterson method imposes less stringent requirements upon the quality and quantity both of single-crystal and powder experimental data. It was demonstrated[2] that direct methods enable one to find a solution based on the $\{F_{hkl}^2\}$ set comprising 50% of the complete data set, whereas 20% and sometimes even 10% of the complete data set would suffice to find a solution by the Patterson method. Reflections, which cannot be reliably separated, are generally rejected.

As a rule, the Patterson method is applicable to structures containing one or several heavy atoms and, hence, it cannot, at first glance, be used for the solution of crystal structures of organic compounds, which contain no atoms heavier than O. However, this is not true for structures containing a known structural fragment. By comparing all calculated interatomic vectors in this fragment, one can attempt to find first the orientation and then the position of this fragment in the unit cell based on analysis of three-dimensional Patterson maps. This procedure is successfully realized in the DIRDIF,[102] PATSEE,[103] and ROTSEARCH programs.[104–106] The latter program was used for localization of three independent $C_{16}H_{22}N_6$ molecules in the hexagonal unit cell based on powder data measured on a laboratory diffractometer.[107]

Systematic search method. The systematic search for a molecule or a molecular fragment of the known structure consists in the systematic analysis of all possible positions and orientations of this fragment in the unit cell. This method is based on apparent principles and is rather simple.[45,108–114] Let us consider one of the possible applications of this method.[113,114] The position of a molecule or a group of atoms with the known geometry in the crystallographic cell can be described by the polar angles ψ, ϕ, and κ [115,116] and the translation vector $\boldsymbol{t}$. Hence, it follows that structure factors for such a crystal structure can be expressed in terms of these parameters, *i.e.*, $F_{\text{calc}} = F_{\text{calc}}(\psi, \phi, \kappa, \boldsymbol{t})$. At the stage III, the set of $\{X_{\text{exp}}\}$ can be obtained by decomposing the powder pattern into integrated intensities of individual peaks

$$X_{\text{exp}} = \Sigma m_i F_{\text{exp},i}^2 = S\Sigma m_i Y_i F_{\text{calc},i}^2 = SX_{\text{calc}}, \qquad (5)$$

where $i = 1$ in the case of an individual peak, whereas i has several values in the case of overlapping reflections. Figure 1 shows a fragment of a powder pattern containing several diffraction peaks to which ten reflections (six well-resolved reflections and four overlapping reflections) make contributions. In this case, the decomposition of the powder pattern into integrated intensities gives eight X_{exp} values, *viz.*, six individual values for which $i = 1$ and two X_{exp} values for which $i = 2$, *i.e.*, each of the latter two values is a sum of the contributions of the intensities of two overlapping reflections. In Eq. (5), m_i is the multiplicity of the i-th reflection, Y_i corresponds to the texture correction multiplier, and S is the normalizing factor calculated from the condition

$$\Sigma(X_{\text{exp},j} - SX_{\text{calc},j})^2 \to \min \qquad (6)$$

for given ψ, ϕ, κ, and $\boldsymbol{t}$. The texture correction multiplier Y_i is generally taken equal to unity; however, in some cases where the character of the texture is known, this multiplier can take particular values, which makes the structure solution much easier. Each arrangement of the molecular fragment is characterized[113,114] by the R factor

$$R(X) = \Sigma|X_{\mathrm{exp},j} - SX_{\mathrm{calc},j}|/\Sigma X_{\mathrm{exp},j} \qquad (7)$$

whose minimum corresponds to the "true" position of the molecule in the crystal lattice or, to put it differently, is indicative of the correct structure solution. Relationships (5)—(7) virtually correspond to the Rietveld full-profile refinement of the crystal structure and enable one to treat the intensities of overlapping reflections without their separation into individual components. The essential advantage of this approach is a sharp decrease in the number of experimental values due to the use of $\{X_{\mathrm{exp}}\}$ sets instead of $\{y_{\mathrm{exp}}\}$ sets, which makes it possible to reduce the time of calculations by an order of magnitude.

It should be noted that the essence of the systematic search method consists in the algorithm for the minimization of the R factor rather than in a particular form of the latter. To search for the minimum of $R(X)$, the six-dimensional region of the possible values of the ψ, ϕ, κ, and $\boldsymbol{t}$ parameters was covered[113,114] with a discrete grid with a given step. For each point of this grid, the value of $R(X)$ was calculated and its minimum was indicative of the possible solution. It is significant that this procedure[113,114] can involve the subsequent Rietveld refinement, which allows one to find out whether the minimum is global or local.

How should the discrete grid be chosen in the systematic search? It is reasonable that smaller translational and rotational steps are preferable because this raises the probability that the global minimum will be found, and that is actually the case. However, it should be taken into account that the number of the orientations and positions to be examined (and hence, the time of calculations) sharply increases as the step of the grid is decreased. Presently, it seems reasonable to use the grid, which covers the asymmetric unit with a step of 0.6—0.8 Å for each atom of the structural fragment both in the case of translations and rotations, since the structural fragment can be shifted from the true position by approximately this value (~0.7 Å). Meanwhile, this shift is then compensated in the course of the Rietveld refinement using restrictions imposed on the bond lengths and bond angles. In some cases, the number of trial models can be sharply decreased by performing simple geometric analysis. For example, in the crystal structure of the dye $C_{18}H_{12}O_2$[117] whose molecule is obviously planar, the parameter c of the monoclinic unit cell is 3.990 Å. Since intermolecular distances in stacks of such molecules are generally in the range of 3.3—3.6 Å, the angle between the normal to the molecular plane and the axis c of the unit cell should be in the range of 20—40° (Fig. 2). Taking into account this restriction, the number of trial models is decreased by a factor of 50.

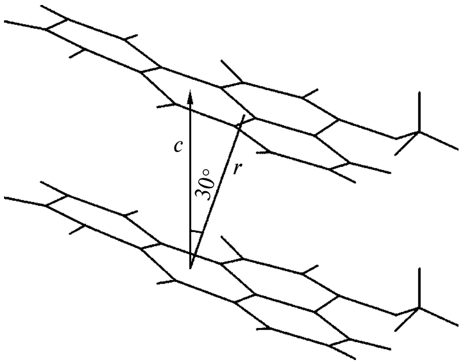


Fig. 2. Geometric restrictions imposed on the possible orientations of the $C_{18}H_{12}O_2$ molecules[117] in the orthorhombic unit cell with the parameter c = 3.990 Å; r = 3.46 Å is the interplanar distance in the stacks of the molecules.

The solution of the triclinic structure of $C_{60}Br_{24}(Br_2)_2$ [111] and the determination of the structure of mesogenic diol $C_{24}H_{34}O_4$ [118] based on synchrotron powder data demonstrate the present-day possibilities of the systematic search method as applied to the structure determination from powder data.

Monte Carlo method and its modifications. Monte Carlo methods are used virtually in all fields of modern science, which employ computer simulation of various processes. The main advantage of these methods is the fact that they enable one to deal with functions, which depend on a large number of parameters, within a reasonable time scale. The algorithm of the Monte Carlo method, as applied to the structure determination from powder diffraction data, can be described as follows. Let us search for the minimum of the function R, which depends on the set of parameters $\mathbf{P} = \{p_1, ..., p_n\}$. Any function containing F_{hkl}^2, for example, $R(X)$ in the form of Eq. (7) or the profile functions R_{wp} or χ^2 (described below in Section VI), can be taken as the function R to be minimized. The parameters $\mathbf{P}$ can include, for example, translational and orientational parameters of one or several structural fragments as well as torsion angles, bond lengths, and coordinates of certain atoms. Initially, the parameters $\mathbf{P}$ are assigned arbitrary values $\mathbf{P}_0 = \{p_1{}^{(0)}, ..., p_n{}^{(0)}\}$ from which the value of the function $R(\mathbf{P}_0)$ is calculated after the determination of the scale factor. For example, in the case of one structural fragment, the latter is placed with an arbitrary orientation in an arbitrary position in the asymmetric part of the unit cell, which makes it possible to calculate F_{hkl}^2, determine the scale factor, and calculate the R factor. Then a set of test values of the parameters $\mathbf{P}_{\mathrm{test}}$ is generated iteratively by adding random increments to the previous values of the parameters (the values from the set $\mathbf{P}_0$ are used as the starting parameters). At the i-th step of this process, the j-th parameter from the set $\mathbf{P}_{\mathrm{test}}$ is calculated from the value of this parameter from the set $\mathbf{P}_{i-1}$ obtained at the previous step

$$p_{j,\mathrm{test}}{}^{(i)} = p_j{}^{(i-1)} + r_j\Delta p_j, \qquad (8)$$

where r_j is the random value whose absolute value is at most unity and Δp_j is the preassigned maximum possible increment of the j-th parameter. For the new set $\mathbf{P}_{\text{test}}$, $R(\mathbf{P}_{\text{test}})$ and $\Delta = R(\mathbf{P}_{\text{test}}) - R(\mathbf{P}_{i-1})$ are calculated. If $\Delta \le 0$, $\mathbf{P}_{\text{test}}$ are taken as $\mathbf{P}_i$. If $\Delta > 0$, $\mathbf{P}_{i-1}$ are taken as $\mathbf{P}_i$ with the probability $1 - \exp(-\Delta/T)$, *i.e.*, the old values are retained, and the set $\mathbf{P}_{\text{test}}$ is taken with the probability $\exp(-\Delta/T)$, the latter being characterized by the higher value of the R factor compared to that for $\mathbf{P}_{i-1}$. The fulfillment of the latter condition provides a possibility of leaving a local minimum in the course of random wandering. In this algorithm, the parameter T can be considered as an analog of the temperature. Its value is preassigned and it is either held constant (as in the case of the classical Monte Carlo method) or decreases with time (as in the *simulated annealing* method). Presently, no unambiguous criteria are available for choosing optimum values of the parameter T and the maximum increments of the parameters Δp_j in Eq. (8). It is recommended to perform this procedure so as to obtain the reasonable ratio of the number of new values $\mathbf{P}_i$ (*i.e.*, those different from $\mathbf{P}_{i-1}$) to the number of the test values $\mathbf{P}_{\text{test}}$, which is generally 30—40%, and it is also advised to make provision for obtaining test parameters throughout the region of the allowable values. Applications of the classical Monte Carlo method to the structure determination from powder diffraction data were described in many studies.[119—123]

Simulated annealing is actively used in the structure determination from powder data.[35,124—128] It is easy to appreciate the essence of this method following the analogy with the process of formation of a solid from a melt.[35] Let us consider two states of the solid, *viz.*, crystalline and amorphous. At a temperature above the melting point, the atoms move chaotically and the total energy of the system is high. The energy minimum of the system corresponds to the crystalline state. The intermediate value of the energy corresponds to the amorphous state. Two temperature modes for the preparation of a solid from a melt are possible, *viz.*, gradual and immediate cooling. In the case of immediate cooling, atoms are "frozen" in an arbitrary configuration whose energy is far from the minimum value giving rise to an amorphous phase. In the case of gradual cooling corresponding to annealing, the chaotic movement of atoms gradually slows down, which allows the system to choose the optimum configuration with the minimum energy corresponding to the crystalline state. To complete the analogy, let us revert to simulated annealing as applied to the structure determination from powder data where the structural parameters or the degrees of freedom $\mathbf{P}$ correspond to the positions of the atoms in the melt, any one of the R factors corresponds to the energy, and the gradually decreasing parameter T corresponds to the temperature. Simulated annealing is a powerful tool for the structure determination from powder data, which enables one to establish structures of compounds possessing a large number of degrees of freedom. For instance, 79 degrees of freedom were varied in the study[129] of the crystal structure of a solid electrolyte in the polymeric matrix $\mathrm{PEO_6 \cdot LiAsF_6}$ containing 50 non-hydrogen atoms per asymmetric unit. The determination of the structures of synthetic β-haematin[130] and two polymorphs of telmisartan $C_{33}H_{30}N_4O_2$ [131] provide impressive examples demonstrating the possibilities of simulated annealing.

The *genetic algorithm*[132—135] employed for the generation of new values of the parameters $\mathbf{P}_i$ can be considered as an interesting adjunct to the Monte Carlo method as applied to the structure determination from powder data. At the i-th step, this method operates with a group of vectors $\{\mathbf{G}_i\} = \{\mathbf{P}_{1i}, \ldots, \mathbf{P}_{mi}\}$ (rather than with one vector $\mathbf{P}_i$) associated with a population consisting of the vectors $\mathbf{P}_{ki}$. By analogy with the evolution of populations in nature, the population $\{\mathbf{G}_i\}$ is allowed to evolve through subsequent generations, *i.e.*, on going from the i-th to $(i + 1)$-th step. The fitness of the population is estimated by the R factor for each member, *viz.*, $R(\mathbf{P}_{ki})$. In the course of evolution, parents, *viz.*, vectors from the i-th generation, mate with each other and impart useful properties (variable parameters minimizing $R(\mathbf{P}_{ki})$) to offsprings, *viz.*, to the vectors from the $(i + 1)$-th generation; however, random mutations can also take place. Figuratively speaking, this algorithm models natural selection and, at a particular evolution step, allows one to obtain the vector $\mathbf{P}_{ki}$ corresponding to the structure solution sought. The genetic algorithm, as applied to the structure determination from powder data, was detailed in the study.[135] The genetic algorithm is realized in the GAPSS program[135,136] and its successful application can be demonstrated with the determination of the crystal structure of steroid $C_{25}H_{31}F_3O_5S$ [137] from powder data measured on a laboratory diffractometer.

Model location from crystal packing considerations. Gradually developing methods for the model location from crystal packing considerations can provide an essential support for the solution of molecular crystal structures from powder data. In such calculations,[138—152] the crystal packing energy is generally minimized using rigid molecules (sometimes, a small number of internal degrees of freedom are allowable). Differences in approaches are, as a rule, associated with particular expressions used for calculations of the packing energy. For these methods, the stages II and III (see Scheme 1) are not necessary because the unit cell parameters and symmetry can be determined from the results of model location from crystal packing considerations. Hence, the theoretical powder pattern can be constructed and compared with the experimental pattern or it is possible to perform the Rietveld refinement of the model obtained. It should be noted that theoretical calculations involving minimization of the packing energy are time consuming. This time can be reduced by performing the stages II and III and preassigning the unit cell parameters and symmetry. The latter approach allowed successful determination of the structures of the metastable phase of piracetam $C_6H_{10}N_2O_2$ [153] and yellow pigment $C_{18}H_{10}N_2O_3$ [154] based on powder diffraction data.

Although these computational methods, as applied to the solution of new crystal structures, gave only modest results,[151] they seem to be promising. These methods would be expected to be not only a unique tool in establishing the structures of the already synthesized compounds but also useful in predicting possible polymorphs of these compounds, which is of particular importance in the design of pharmaceuticals and their patenting. Computational methods for the model location from crystal packing considerations were described in more detail in the reviews.[151,155]

V. Structure completion

In some cases, the results of the stage IV of SDPD make it possible to establish the structure and determine the coordinates of all atoms in the asymmetric part of the unit cell, which allows one to immediately proceed to the final VI stage, *viz.*, to the structure refinement. However, the stage IV generally gives the positions only of some atoms or even of one heavy atom (for example, using the Patterson method). In the latter case, by analogy with single-crystal studies, the lacking atoms are localized from difference Fourier maps using $|F_{\text{exp}}|$ obtained at the stage III and F_{calc} calculated from the positions of the atoms revealed at the stage IV. Difference electron density maps can be calculated using either program packages for single-crystal studies or some program packages for powder X-ray strudies, *viz.*, GSAS [69] and FULLPROF.[68]

The lacking structural fragments can be efficiently revealed using the above-mentioned systematic search method or the Monte Carlo methods. This approach is often the only possible way of locating structural fragments, particularly, when the presence of numerous overlapping reflections in the powder patterns hinders the reliable determination of $|F_{\text{exp}}|$, which, in turn, results in noninterpretable difference electron density maps. For example, when solving the structures of Pd(Phen)(C(O)N(Me)OC(O)) [156] and $C_9H_{16}N_5O_2{}^+Cl^- \cdot H_2O$,[157] the position of the heavy atom (Pd and Cl, respectively) was initially determined by the Patterson method and then the positions and orientations of the remaining molecular fragments were revealed by the systematic search method.

VI. Rietveld refinement of the crystal structure

We have already mentioned the Rietveld full-profile refinement[3,4] when considering the stage III of SDPD. In essence, this method is based on the minimization of functional (4) in which the calculated scattering intensity $y_{\text{calc}}(i)$ is described by Eq. (3). The Rietveld refinement differs radically from the powder pattern decomposition into integrated intensities used at the stage III in that the Rietveld refinement involves the usual structural parameters of X-ray diffraction analysis, *viz.*, atomic coordinates, occupancies of atomic positions, and thermal parameters, as variable parameters. In the Rietveld refinement, squared structure factors $F_{hkl}{}^2$ are no longer independent variables and they are calculated from the variables at each iteration. The total list of variable parameters in the Rietveld refinement is rather large. In addition to the structural parameters we are primarily interested in, this method allows the refinement of variables specifying the profiles and half-widths of diffraction peaks, the unit cell parameters, the texture parameters, the background parameters, and some other characteristics. The detailed description of the Rietveld method is beyond the scope of the present review because this approach has been covered comprehensively in the monograph[62] and reviews.[63,158,159] Let us only present the commonly accepted expressions for the profile (R_p) and weighted profile (R_{wp}) R factors characterizing the quaility of the refined data:

$$R_p = \Sigma|y_{\text{exp}}(i) - Sy_{\text{calc}}(i)|/\Sigma y_{\text{exp}}(i), \tag{9}$$

$$R_{wp} = \{\Sigma w_i[y_{\text{exp}}(i) - Sy_{\text{calc}}(i)]^2/\Sigma w_i[y_{\text{exp}}(i)]^2\}^{1/2}, \tag{10}$$

$$R_{\text{exp}} = \{(N - P)/\Sigma w_i[y_{\text{exp}}(i)]^2\}^{1/2}, \tag{11}$$

$$\chi^2 = R_{wp}/R_{\text{exp}}, \tag{12}$$

where N is the number of the measured points and P is the number of refinable parameters.

The Rietveld method is realized in numerous programs, for example, in CSD,[66] DBWS,[160] FULLPROF,[68] GSAS,[69] MRIA,[71] POWSIM,[93] PROFIL,[72] RIETAN,[161] and XRS.82.[162] As mentioned above, the structure determination from powder data differs radically from single-crystal X-ray diffraction analysis in that the number of independent observed parameters in the former case is substantially smaller, whereas the number of variable parameters remains the same or even increases. Hence, the treatment of particular groups of atoms as rigid fragments with fixed geometry, which are refined as rigid bodies (for example, by varying only one torsion angle), or restrictions imposed on the bond lengths and bond angles[163] and the fixed planarity of particular structural fragments are important attributes of many programs, which enhance stability of the refinement.

What are the desired values of the R factors described by Eqs. (9)—(12)? In the ideal case, the refinement is completed when $\chi^2 = 1$. In practice, the χ^2 parameter varies over a rather wide range for a variety of reasons, for example, due to an inadequate peak shape function, the complex character of the texture, or, finally, the incorrect structure solution. Hence, the convergence of the Rietveld refinement of a particular model (as in the case of single-crystal X-ray diffraction analysis) is determined by the ratio $|\Delta_j/\sigma_j|_{\max}$, where Δ_j is the increment of the j-th parameter in the ongoing cycle of the refinement and σ_j is its standard deviation, rather than by the R factors. As soon as $|\Delta_j/\sigma_j|_{\max}$ becomes smaller than ε (ε is generally taken equal to 0.01), the refinement is terminated. To gain an additional visual estimation of the quality of the refinement, it is useful to compare

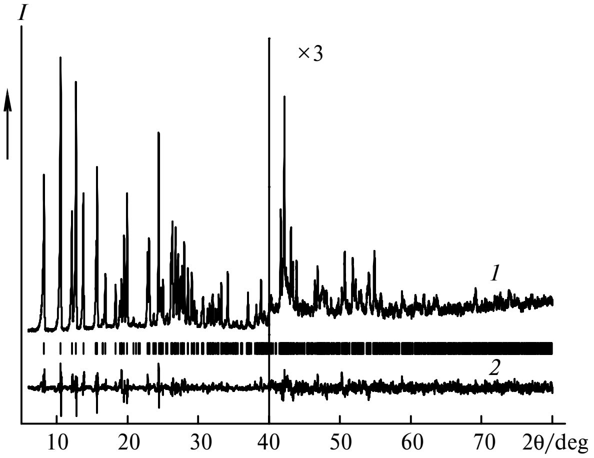


Fig. 3. The results of the Rietveld refinement of the $C_{10}H_{15}N_5O_2S_2$ structure using the diffraction data measured on a Guinier camera:[157] the experimental curve (*1*), the difference between the experimental curve and the curve calculated based on the results of refinement (*2*); the calculated positions of the reflections are indicated by vertical bars.

three curves, *viz*., the experimental and calculated powder patterns and the difference curve, by presenting them in one figure. However, only two curves, *viz*., experimental and difference, are generally reported, the high-angle fragment of the X-ray pattern being drawn on an enlarged scale for clarity (Fig. 3). In such plots, the calculated positions of diffraction peaks of all reflections are also presented (indicated by vertical bars).

The Rietveld full-profile refinement completes the structure determination from powder data. Based on the results of this refinement, a researcher either reverts to the stage V (or even to the stage II) or reasones that the determination of the crystal structure is completed.

Texture and microstructure effects

Before proceeding to examples of structures solved by different methods from powder diffraction data, it is necessary to consider two phenomena, *viz*., the texture and microstructure effects, which can have a pronounced influence on the overall course of the structure determination. These effects must be taken into account because they can change significantly the ratio of the integrated intensities of reflections. This is particularly true for the texture.

When treating powder data, one initially assumes that crystallites in a specimen prepared for measurements are oriented randomly, *i.e*., isotropically, thus allowing all atomic planes with different *hkl* indices to make equal contributions to scattering. This situation can readily be imagined if crystallites are represented as spheres, which fill a particular reservoir, for example, a cell or a capillary. However, crystallites often, in spite of their small sizes (which sometimes are at most 1—5 μm), occur as essentially anisotropic platelets or needles. In these cases, anisotropic crystallites possess special directions, *viz*., the normal to the surface in the case of platelets and the needle axis in the case of needles. Filling of a reservoir with such anisotropic particles can give rise to effects of the preferred orientation (or texture), *i.e*., the distribution of orientations of crystallites within the specimen is not isotropic but has one or several special directions. For example, when platelet-like crystallites are placed into a flat cell followed by surface smoothing (the standard procedure for preparing specimens for many laboratory powder diffractometers operating in the reflection mode with the Bragg—Brentano geometry), the platelets tend to be located parallel to the bottom of the cell. Another example is filling of a narrow capillary of a diameter <0.5 mm with needle-like crystallites (this procedure is used in measurements by the Debye method) when needles are oriented parallel to each other and along the axis of the capillary. For example, such a preferred orientation was observed in the determination of the crystal structure of sodium oxamate $NaC_2O_3NH_2$ from synchrotron powder data.[164] The presence of texture in a specimen corresponds to the preferred contribution of particular atomic planes to scattering and suppression of all other reflections. This can lead to substantial changes in the diffraction pattern. Figure 4 shows three powder patterns of the same dye of composition $C_{18}H_{12}O_2$:[117] a pattern measured on a DRON-3 diffractometer with the Bragg—Brentano geometry from a specimen, which was prepared according to a standard procedure (see Fig. 4, *a*), a pattern measured from the same dye on a Guinier camera in the transmission mode (see Fig. 4, *b*), and a powder pattern (see Fig. 4, *c*), which was also measured on a Guinier camera but from a specimen prepared according to a special procedure to minimize the texture effects (attempts to completely get rid of these effects failed). Only the *hk*0 reflections are observed in Fig. 4, *a*, whereas intense peaks can be seen in Fig. 4, *b* at $2\theta \approx 23°$ where the first reflections with $l \neq 0$ are located.

The texture effects in powders have long been known.[165,166] Various procedures were developed for taking adequate account of these effects in diffraction experiments.[167—173] In the Rietveld method, the March—Dollase function[167] is used successfully and most commonly. This approach requires the assignment of the axis with the preferred orientation and only one refinable parameter. However, it is very desirable to prepare specimens in such a way as to minimize the texture effects, which simplifies the solution and refinement of the crystal structure. Unfortunately, this aim cannot often be achieved. In these cases, one should attempt to determine the direction of texture or the axis of the preferred orientation of the crystallites. This problem can be solved by carrying out measurements both in the reflection and transmission modes thus obtaining two powder patterns with the opposite texture effects. For example, if the *hk*0 reflections are more

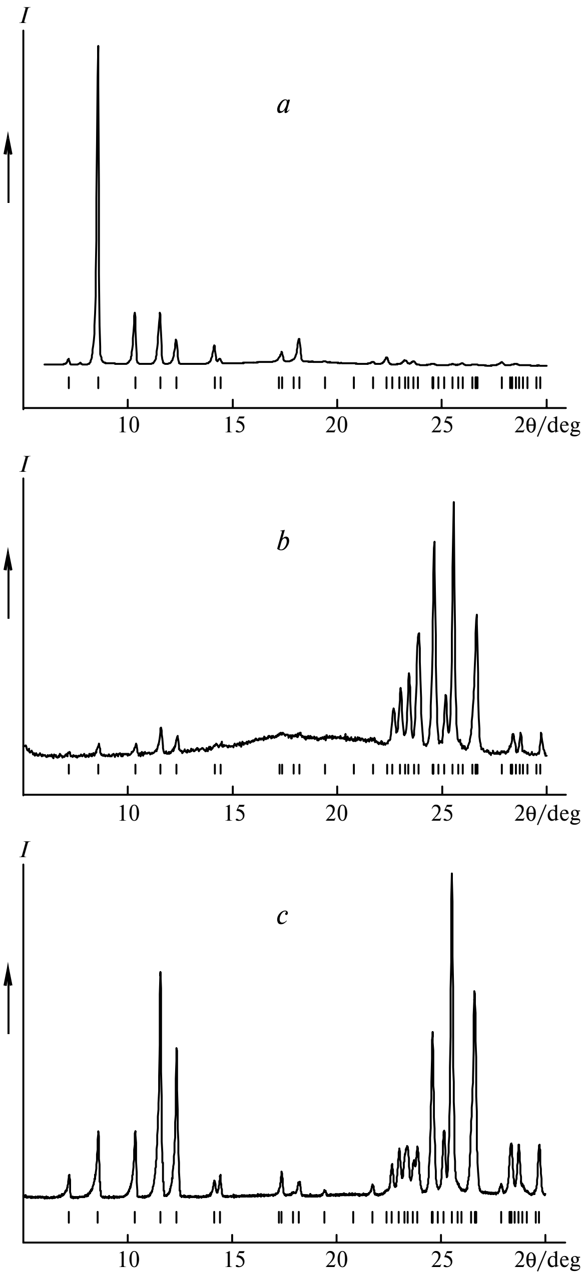


Fig. 4. Texture effect in a specimen of $C_{18}H_{12}O_2$:[117] *a*, a specimen, which was prepared according to a standard procedure and studied on a DRON-3 diffractometer operating in the reflection mode; *b*, the same specimen studied on a Guinier camera in the transmission mode; *c*, a specimen, which was prepared according to a special procedure to minimize the texture effects and studied on a Guinier camera in the transmission mode; the calculated positions of reflections are indicated by vertical bars.

pronounced in the first powder pattern measured from a specimen with an orthorhombic unit cell (see Fig. 4, *a*), reflections with the non-zero index l are more pronounced in the second powder pattern (see Fig. 4, *b*) or vice versa. In some cases, a comparison of two powder patterns makes it also possible to estimate the texture correction multipliers, *i.e.*, the coefficient Y_{hkl} in Eq. (3). It should also be noted that the texture correction multipliers for powders measured in the transmission mode are always smaller that those obtained in the reflection mode[174] and, hence, the transmission mode is preferable for the structure solution.

In recent years, researchers held to the idea that the texture in a specimen is not a side effect, which complicates the structure solution, but serves as a useful ancillary tool. This approach is based on the possibility to quantitatively separate intensities of overlapping reflections using either the controlled texture in specimens,[80,175,176] which are prepared according to different procedures, or highly parallel synchrotron radiation beams and specially designed goniometers.[177] It is obvious that this approach is unique if information on the geometry of the structural fragments is lacking and the structure can be solved based only on a set of F_{hkl}^2 using direct methods or the Patterson method, which require a large number of well-resolved reflections. The determination of the crystal structures of two zeolite derivatives, *viz.*, Mu-9 [177,178] of composition $[Al_{66}(PO_4)_{72}]^{18-}(NMe_4)^+{}_x(NMe_3H)^+{}_y(NEt_2H_2)^+{}_{18-x-y}$ with the unit cell volume of 7254 Å^3 and UTD-1F with the stoichiometry $[SiO_2]_{16} \cdot 0.5[(Cp^*)_2CoF_x(OH)_{1-x}]$ [177,179] ($Cp^* = C_5Me_5$) containing 69 nonhydrogen atoms per asymmetric part of the monoclinic unit cell, with the use of direct methods are prominent examples demonstrating the possibilities of this imaginative approach to the texture whereby intensities for a powder specimen are converted to a well-resolved set for a single crystal. Apparently, the practical realization of these methods is time consuming and requires experimental skill.

Another factor, which is often responsible for substantial changes in diffraction patterns (which are particularly pronounced in powder patterns measured on high-resolution devices), is the existence of the microstructure effects, such as microstrains, anisotropy of the crystallite shape, stacking faults, *etc.* The microstructure effects can be manifested in the anisotropic character of changes in the half-widths of diffraction peaks, unusual peak shapes, or even in the appearance of substantial systematic deviations of their calculated positions from the corresponding experimental values. An adequate mathematical apparatus is necessary for the description of changes in the shapes and positions of the peaks; however, this apparatus is realized in a few programs. This, in turn, can lead to incorrect values of F_{hkl}^2 determined and used in the stages III and VI. Substantial differences in the half-width of two adjacent reflections can be seen in the fragment of the synchrotron powder pattern of the compound $C_6H_6N_6O_4 \cdot H_2O$ [180] (Fig. 5, *a*); the figure also presents the result of the fit of this fragment of the powder pattern assuming that the half-widths of the peaks change isotropically. In this case, anisotropy of the half-widths results from the

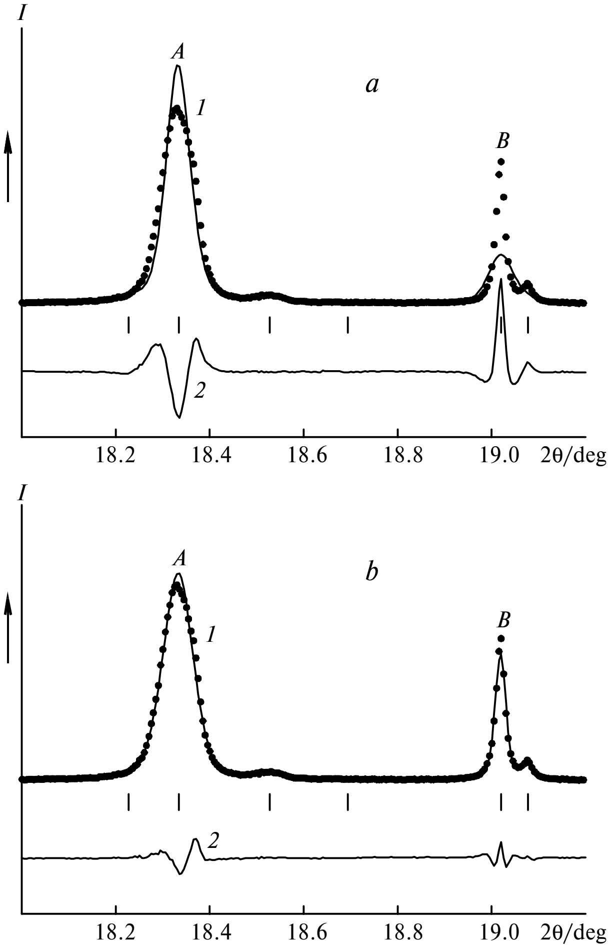


Fig. 5. Fragment of the synchrotron powder pattern of $C_6H_6N_6O_2 \cdot H_2O$ [180] containing peaks of the (321) reflection (2θ = 18.33°, the half-width is 0.077°) (*A*) and the (50—1) reflection (2θ = 19.02°, the half-width is 0.028°) (*B*): the results of the refinement at the stage III assuming that the half-widths of the peaks are changed isotropically (*a*) and anisotropically[181] (*b*); the experimental data are indicated by points, the calculated (*1*) and difference (*2*) patterns are indicated by solid lines; the calculated positions of reflections are indicated by vertical bars.

anisotropic character of microstrains in crystallites, which can be described with the use of the corresponding mathematical apparatus.[181,182] Figure 5, *b* shows the results of the fit of the same fragment of the powder pattern using the formalism,[181] which provides the substantially better agreement between the calculated and experimental data (*cf.* Fig. 5, *a*). The application of this approach[181] to the structure solution of $C_6H_6N_6O_4 \cdot H_2O$ [180] and the more recent method[182] used for the structure solution of sodium *p*-hydroxybenzoate $NaO_2C_7H_4OH$ [183] from synchrotron powder data made it possible to obtain precise values of F_{hkl}^2 at the stage III of SDPD, which allowed the location of the H atoms in the H_2O molecule[180] and the OH fragment[183] from difference electron density maps.

In X-ray powder diffraction studies, the microstructure effects are of importance primarily from the viewpoint of their influence on the structure determination. However, these effects are also of considerable interest for the rapidly developing materials science[184—187] in view of their influence on various properties of many commercial materials.

Examples of structure determination from powder data

Examples of compounds whose crystal structures have been established from powder data (Tables 1 and 2; for other examples, see Ref. 1) convincingly demonstrate the possibilities of the modern SDPD methods, which are actively employed by many research groups for the solution of different problems. Of special note are the determination of the crystal structures of compounds possessing interesting properties with the aim of revealing structure—property relationships. For instance, Table 1 gives examples of high-T_c superconductors,[193] solid electrolytes in polymeric matrices,[125,129] and zeolites[179] (zeolites were also described in the review[213]). Examples of pharmaceuticals,[131,137,153] dyes,[204,210,212] and even the malaria pigment[130] are presented in Table 2.

A knowledge of the crystal structure of a molecular compound is often the only key to establishing the molecular geometry because it allows one to unambiguously choose the solution out of several possible models,[156,180,205,214] which are undistinguishable by spectroscopic and quantum-chemical methods. Starting in the second half of 1990s, considerable progress was achieved in the determination of the crystal structures of organic compounds from powder data due to the intensive development and the use of the Monte Carlo and systematic search methods in SDPD. Information on the crystal structures available in the crystallographic databases, such as the Cambridge Structural Database (CSD)[215] containing complete data on organic compounds and the Inorganic Crystal Structural Database (ICSD),[216] has considerable utility in the structure determination from powder data. These databases include complete structural information (unit cell parameters, space groups, and atomic coordinates) on the crystal structures of hundreds of thousands of compounds. The systematic treatment of a great body of information allows one to construct statistically reliable starting models for the required atomic fragments and to estimate the probabilities of the possible conformations, which, in turn, substantially reduces time consumption at the stage IV of the structure determination from powder data. For organic compounds, the starting molecular models can also be constructed either by molecular mechanics or based on the results of semiempirical quantum-chemical calculations (for example, by the MNDO method[217]) using such programs as PCMODEL [218] or MOPAC.[219]

The details of the solution of the crystal structures listed in Tables 1 and 2 are beyond the scope of the

Table 1. Examples of inorganic and complex compounds whose crystal structures were established from powder data

Compound	Space group	Z	V^a /Å^3	Reference
$(NH_4)_4[(MoO_2)_4O_3](C_4H_3O_5)_2 \cdot H_2O$	*C*2	2	1441	5
$NaHSO_4$	$P2_1/n$	4	334	45
$CuBr_2(C_7H_9N)_2$	$P2_1/a$	2	819	188
α-$CrPO_4$	*Imma*	12	845	20
$FeAsO_4$	$P2_1/n$	4	297	19
$HgBa_2(Eu_{1-x},Ca_x)Cu_2O_7$	$P4/mmm$	2	190	189
Nd_2HgO_4	$C2/m$	4	461	190
C_{60} (T = 5 K)	$Pa\bar{3}$	4	2768	108
τ-AlF_3	$P4/nmm$	16	744	191
$Ga_2(HPO_3)_3 \cdot 4H_2O$	$P2_1$	2	580	192
$HgBa_2CuO_{4+\delta}$	$P4/mmm$	1	143	193
β-Ba_3AlF_9	$Pnc2$	8	1632	194
$[Me_4N]_4Ge_4S_{10}$	$P\bar{4}3n$	8	7471	195
$La_3Ti_5Al_{15}O_{37}$	*Cc*	4	2383	196
RbC_{60}	*Pmnn*	2	1315	109
$C_{60}Br_{24}(Br_2)_2$ (T = 35 K)	$P\bar{1}$	1	1560	111
$(UO_2)_3(HO_3PC_6H_5)_2(O_3PC_6H_5)_2 \cdot H_2O$	$P2_12_12_1$	4	3452	197
$(C_2H_4O)_3[LiN(SO_2CF_3)_2]$	$P2_1/c$	4	1561	125
$Zn_3(OH)_2V_2O_7 \cdot 2H_2O$	$P\bar{3}m1$	1	228	198
$Bi(H_2O)_4(OSO_2CF_3)_3$	$P2_1/c$	4	1386	199
$(C_2H_4O)_6[LiAsF_6]$	$P2_1/a$	4	1825	129
$[SiO_2]_{16} \cdot 0.5[(Cp^*)_2CoF_x(OH)_{1-x}]^b$	$P2_1/c$	4	3718	179
$Fe^{3+}{}_{5.34}(PO_4)_{3.62}(VO_4)_{0.38}(OH)_4 \cdot 6.7H_2O$	$P\bar{1}$	2	505	200

[a] Unit cell volume.

[b] Cp* is pentamethylcyclopentadienyl C_5Me_5.

present review. In each case, the structure solution involved the stages I—VI. Methods for the structure determination from powder data often allow one to find the solution in complicated cases when it is impossible to get rid of impurity phases in the specimen under study. Thus, the specimen of $HgBa_2(Eu_{1-x},Ca_x)Cu_2O_7$ used for the determination of its structure[189] contained four impurity phases; however, all these phases were identified and taken into account so that their presence did not hinder the structure solution. Similarly, the presence of the known Et_3NHCl phase in the specimen did not hinder the determination[209] of the mesoionic structure of $C_{14}H_9NO_3$. In some cases, the problems of the stages II—VI of the structure determination were successfully solved based on powder data for two-phase specimens, *i.e.*, two new crystal structures were simultaneously established from a single powder pattern. Examples are the structures of two polymorphs of $Rb(C_5H_5)$ [220] as well as the structures of $Me_2SBr_{2.5}$ and Me_2SBr_4.[221] The possibilities of the modern methods for the structure determination from powder data can also be demonstrated by the solution of disordered crystal structures, for example, of LiCp* (see Ref. 203) and $(Fc)_2C{=}C{=}C{=}C(Fc)_2$.[207] Noteworthy also are first studies in which the protein structures of whale metmyoglobin[222] and the T_3R_3 human insulin-zinc complex[60] were established based on synchrotron powder data.

Table 2. Examples of organic and organometallic compounds whose crystal structures were established from powder data

Compound	Space group	Z	V^* /Å^3	Reference
$C_6H_{10}N_2O_2$	$P2_1/n$	4	723	153
CH_3F (T = 5 K)	$P2_1/n$	4	187	201
$C_{16}H_{22}N_6$	$P3$	3	1209	107
C_6H_5Li	$P2_1/n$	4	498	202
$C_{15}H_{11}N_3O_3Pd$	$Pn2_1a$	4	1310	156
$C_9H_9N_3O_2S$	$P2_1/n$	8	2285	101
$C_{18}H_{10}N_2O_3$	$Pna2_1$	4	1330	154
$C_{25}H_{31}F_3O_5S$	$P2_12_12_1$	4	2486	137
$Li[C_{10}H_{15}]$	$R3m$	3	722	203
$C_{18}H_{12}O_2$	$P2_12_12_1$	4	1250	204
$C_9H_{10}N_4O_3 \cdot H_2O$	$P2_1/a$	4	1074	205
$[C_{12}H_{26}N_4]^{2+}[Cl^-]_2$	$P2_1/n$	2	746	206
$C_{44}H_{36}Fe_4$	$P2_1/a$	1	814	207
$C_{34}H_{32}N_4O_4Fe$	$P\bar{1}$	2	1416	130
$C_{27}H_{18}AlN_3O_3$	$P\bar{1}$	2	1111	208
$C_{33}H_{30}N_4O_2$	$P2_1/c$	4	2701	131
$C_{33}H_{30}N_4O_2$	$P2_1/a$	4	2764	131
$C_{14}H_9NO_3$	$Pna2_1$	4	1054	209
$[C_{12}H_{12}N_3]^+Cl^-$	$P2_1/c$	4	1134	210
$C_{14}H_8N_2O_5$	$P2_1/n$	4	1190	211
$[C_{16}H_{14}N_3]^+Cl^-$	$P2_1/c$	4	1380	212

* Unit cell volume.

The determination of ten structures of aromatic compounds[223,224] from powder data measured on laboratory devices seems to be a rather modest achievement against the background of the above-considered examples. However, these systematic routine studies lend credibility to the results obtained from powder diffraction data.

Measuring devices and reproducibility of results

In the above-considered examples, the crystal structures were established based on powder patterns, which were measured on different diffractometers using radiation of different types. This raises the questions as to the dependence of the structure solution on the device used for data collection and as to whether the results are adequately reproduced on going from one type of radiation to another. These questions were considered[180] in the solution and refinement of the structures of two heterocyclic compounds with the stoichiometry $C_7H_{11}N_5O_2$ and $C_6H_6N_6O_4$ based on powder data, which were measured on three different (laboratory X-ray, synchrotron X-ray, and neutron) diffractometers. It was demonstrated[180] that the results of the determination of the above structures are rather well reproduced. The investigation based on synchrotron powder data required the shortest time because the high-quality experimental data made it possible to find the solution by direct methods based on the $\{F_{hkl}^2\}$ set extracted at the stage III (see Scheme 1). However, it should be remembered that synchrotron and neutron measurements are carried out only in the major scientific centers and, hence, researchers sometimes have to wait several months for an access to apparatus.

A comparison of the possibilities of different powder diffractometers in the solution of crystal structures (Table 3)[225] demonstrates that synchrotron measurements are preferable in every respect. Of laboratory diffractometers, devices operating in the transmission mode and using only the $K\alpha_1$ component of the characteristic radiation are best suited for determining crystal structures. At the same time, it should be noted that the differences in the intensity data measured on different devices are of lesser importance in the refinement of the already solved structures compared to the other stages. Hence, virtually all diffractometers (see Table 3) can be used for the determination of structures of different complexity. Highly reliable results can be obtained on different devices. For example, the latter conclusion can be confirmed by the determination of the structures of $[C_{12}H_{12}N_3]^+Cl^-$ (see Ref. 210) and $[C_{16}H_{14}N_3]^+Cl^-$ (see Ref. 212) in which the stages II—VI were carried out based on powder patterns measured on a DRON-3 diffractometer.

It is reasonable that the accuracy of the results obtained from powder data is much lower than that obtained in single-crystal studies. For example, chemical bond lengths are generally determined from single-crystal X-ray diffraction data with an accuracy to the third decimal place (for the values determined in Å), whereas the accuracy of these parameters determined from powder data are 5—10 times lower.[226—228] In addition, powder data, particularly those measured on laboratory devices, unlike single-crystal diffraction data, are virtually "insensitive" to the positions of H atoms. Hence, supplementary information in addition to the bond lengths and bond angles is often required for the correct interpretation of the results obtained from powder data. For instance, in the study,[210] the position of the H atom at one of two possible N atoms was revealed only by analyzing the Cl···N distances. Another factor, which impairs the reliability of the results of the structure determination from powder data, is the use of restrictions imposed on the allowable bond lengths and bond angles at the stage VI. On the one hand, these restrictions help in establishing the true conformation of the atomic fragment in the course of refinement even in the presence of pronounced texture;[180] however, on the other hand, these restrictions may introduce errors into the results obtained. In the special study devoted to this problem,[228] the positions of the atoms in the molecule

Table 3. Comparison of the possibilities of various powder diffractometers in the structure determination from powder data (the highest mark is 5)

Diffractometer	Amount of the compound required for measurements	Indexing	Determination of the space group	Data extraction F_{hkl}^2	Texture effects	Rietveld refinement
DRON-3[a]	3	3	3	3	2	4
Guinier camera[b]	4	5	4	3	3	4
G4.2[c]	2	2	2	2	4	4
BM16[d]	5	5	5	4	5	5

[a] A laboratory X-ray diffractometer, a Ni filter, the reflection mode.

[b] A Guinier—Johanson camera equipped with a curved monochromator, Cu-$K\alpha_1$ radiation, the transmission mode.

[c] A neutron diffractometer with a constant wavelength was designed at the Petersburg Nuclear Physics Institute of the Russian Academy of Sciences (Gatchina, Russia) and exploited at the Leon Brillouin Laboratory (Saclay, France), the transmission mode.

[d] The X-ray diffractometer at the ESRF (European Synchrotron Radiation Facility, Grenoble, France), the transmission mode.

of *m*-fluorobenzoic acid $C_7H_5FO_2$ were refined without restrictions based on synchrotron powder patterns measured at two temperatures (295 and 100 K). It was demonstrated that the Rietveld refinement of the structure using low-temperature data can be carried out for all atoms, including the H atoms, without restrictions on the allowable bond lengths. At the same time, these restrictions must be used in the refinement based on the diffraction data measured at room temperature.[228]

In the design of experimental studies aimed at establishing an unkown crystal structure, one should realize the expected accuracy of the results, *i.e.*, judge as to whether the accuracy will be high enough for the goal of the study to be accomplished. If these questions are posed and solved before the beginning of the study, the results can be obtained with the smallest time consumption.

Estimation of the correctness of the structure determination

How can one estimate the reliability of the solution obtained? The question is also arises as to whether this solution corresponds to the global or local minimum. It should be noted that no commonly accepted reliable criteria are presently available, which can allow unambiguous conclusions about the correctness of the solution found. The requirements are only that the structure must be chemically adequate, *viz.*, the bond lengths, bond angles, and crystal packing must be reasonable, and the results must be in complete agreement both with NMR and IR spectroscopic data and the data from mass spectrometry. In most of investigations dealing with the structure determination from powder data, the reported *R* factors (9)—(12) were obtained at the final stage (VI) of the Rietveld refinement. However, the absolute values of the profile *R* factors are by themselves poorly informative. A comparison of the R_{wp} factors for several structures, which were solved from powder data measured on different diffractometers, (Table 4)[229] demonstrates that the absolute values of the *R* factors obtained in the Rietveld refinement are substantially different not only for different devices but also for different compounds measured on the same device. Table 4 also gives the R_{wp} factors determined at the stage III after decomposition of the powder patterns into integrated intensities. As mentioned above (this fact was noted in many studies[64,65,196,230]), the *R* factors (9)—(12) determined at the stage III have the smallest values possible for a particular unit cell and space group. Hence, these values can serve as a limit, which one should strive to achieve at the stage VI of the structure determination. Actually,

Table 4. Comparison of the profile R_{wp} factors after the stages III and VI for various compounds and different powder diffractometers

Diffractometer*	Compound	$(R_{wp})_{III}$	$(R_{wp})_{VI}$	$(R_{wp})_{VI}/(R_{wp})_{III}$	Reference
DRON-3	*p*-Phenylazoaniline hydrochloride ($[C_{12}H_{12}N_3]^+Cl^-$)	0.037	0.040	1.1	210
	1-Naphthyl-4-phenylazoamine hydrochloride ($[C_{16}H_{14}N_3]^+Cl^-$)	0.048	0.052	1.1	212
	3-Amino-6-methyl-4-nitro-8-oxopyrazolo[1,5-*a*]pyrimidine ($C_7H_7N_5O_3$)	0.057	0.059	1.0	214
	3-Amino-6,8-dimethyl-4-nitropyrazolo[1,5-*a*]pyrimidine ($C_8H_9N_5O_2$)	0.065	0.069	1.1	214
Guinier camera	2,6-Diamino-5-hydroxy-3-nitro-4*H*-pyrazolo[1,5-*a*]-7-pyrimidone monohydrate ($C_6H_6N_6O_4 \cdot H_2O$)	0.055	0.065	1.2	180
	2-[1-(2-Aminoethyl)-2-imidazolidinylidene]-2-nitroacetonitrile ($C_7H_{11}N_5O_2$)	0.074	0.077	1.0	180
	2-Chloro-1-(*p*-nitrophenacyl)pyridinium bromide ($[C_{13}H_{10}N_2O_3Cl]^+Br^-$)	0.076	0.080	1.1	128
	6-Dimethylamino-5-nitro-4-pyrimidine *N,N*-diethyldithiocarbamate ($C_{11}H_{10}N_2O_3S_2$)	0.088	0.098	1.1	157
	3-Methoxybenzoanthrone ($C_{18}H_{12}O_2$)	0.100	0.116	1.2	117
G4.2	2-[1-(2-Aminoethyl)-2-imidazolidinylidene]-2-nitroacetonitrile ($C_7H_{11}N_5O_2$)	0.011	0.012	1.1	180
	2,6-Diamino-5-hydroxy-3-nitro-4*H*-pyrazolo[1,5-*a*]-7-pyrimidone monohydrate ($C_6H_6N_6O_4 \cdot H_2O$)	0.013	0.016	1.2	180
	3-Amino-6-methyl-4-nitro-8-oxopyrazolo[1,5-*a*]pyrimidine ($C_7H_7N_5O_3$)	0.020	0.023	1.2	214
BM16	2-[1-(2-Aminoethyl)-2-imidazolidinylidene]-2-nitroacetonitrile ($C_7H_{11}N_5O_2$)	0.059	0.064	1.1	180
	2,6-Diamino-5-hydroxy-3-nitro-4*H*-pyrazolo[1,5-*a*]-7-pyrimidone monohydrate ($C_6H_6N_6O_4 \cdot H_2O$)	0.065	0.068	1.0	180
	Sodium oxamate ($NaC_2O_3NH_2$)	0.080	0.085	1.1	164

* The diffractometers are described in Table 3.

the ratios of $(R_{wp})_{VI}$ obtained at the stage VI to $(R_{wp})_{III}$ obtained at the stage III are approximately equal (~1.2) in all the cases listed in Table 4. The Rietveld refinement without restrictions on the geometric parameters of the structure can be useful in checking the correctness of the solution. In the case of the global minimum, the starting structure remains stable although the refinement can lead to substantial distortions of the bond lengths and bond angles. Based on the above-considered arguments, three empirical rules were stated,[229] which help in estimating the reliability of the solution obtained: 1) the solution must be in complete agreement with the results of other physicochemical studies; 2) the relationship $(R_{wp})_{VI}/(R_{wp})_{III} < 1.3$ must be fulfilled for the solution to be correct; 3) the Rietveld refinement of the structure without fixation of structural fragments must converge and may not lead to crucial changes in the atomic parameters.

Of the above-mentioned conditions, only the second condition involves quantitative relationships; however, it is desirable to check all three conditions because they can sometimes be indicative of possible directions of a search for the correct solution. For example the solution, which was obtained in the structure determination of $C_6H_6N_6O_4$ (the monoclinic unit cell with a volume of 894 Å^3) from powder data measured on a laboratory diffractometer,[180] completely satisfied the first and third conditions but was inconsistent with the second condition. After several unsuccessful attempts to reduce the value of $(R_{wp})_{VI}$ at the stage VI using various possible conformations of the starting molecule and texture models, it was assumed that the unit cell contains water of crystallization. Initially, this possibility was ignored because the crystal packing seemed to be rather dense (the volume increment of the nonhydrogen atom in the crystal packing was equal to 14 Å^3). However, when this assumption was examined at the stage V, the O atom (corresponding to H_2O) was revealed in the difference Fourier map and after the refinement of its position, the second condition was met.

Internet resources

The gradual development of the global Internet network opens up a broad spectrum of possibilites for researchers. For example, Internet allows one to get acquainted with new methods for the structure determination from powder data. Thus, one can find extensive bibliography on different sites[1] and gain access to program packages[1,231—235] and powder diffraction data measured on different devices.[1] Moreover, special Internet courses are already available for training in the crystal structure determination from powder data.[236] The sites of such organizations as the International Unit of Crystallography (IUCr)[237] and the International Centre for Diffraction Data (ICDD)[238] can also be useful for these purposes.

* * *

One would expect that methods for the structure determination from powder data will be intensively evolved. The development of these methods is stimulated by the fact that they enable one to obtain the required results with minimum resource consumption among which time is the most important factor. Actually, single-crystal X-ray diffraction analysis has advantages over X-ray powder studies because the accuracy of the results obtained in the latter case are much lower. However, the search for the conditions of crystallization of single crystals of appropriate sizes may take many years, whereas the determination of the same structure from powder data (from the measurement of the powder pattern to the structure solution) is often completed in several hours. Hence, researchers are pining hopes on the structure determination from powder data. Besides, many laboratories possess all necessary devices, *viz.*, powder diffractometers and personal computers with an access to the Internet, and these devices are ready to use for the solution of topical problems of SDPD.

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